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Supporting Information for

A NbO-type copper metal–organic framework decorated with carboxylate groups exhibiting highly selective CO_2 adsorption and separation of organic dyes

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1. Materials and Methods

1.1 Synthesis of materials

(a) Ligand H_5L

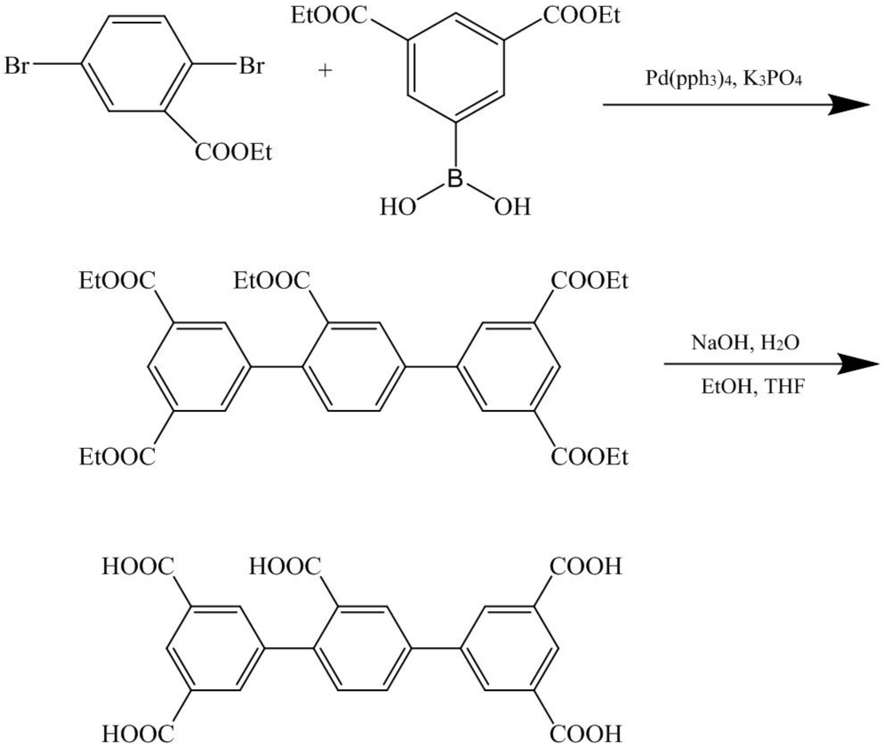


Fig. S1 Synthetic route of $\mathbf{H_5L}$.

The ligand $\mathbf{H_5L}$ (2,5-bis(3’,5’-dicarboylphenyl)-benzoic acid) was synthesized according to the similar procedure described in the literature.[1] $\mathbf{H_5L}$ was synthesized via Suzuki-coupling reaction of 2,5-dibromobenzoic acid ethyl ester and 3,5–diethyllisophalate-5-boronic acid (Fig. S1). 2,5-dibromobenzoic acid ethyl ester (3.07 g, 10 mmol), 3,5-dicarboxyethylester-phenylboronic acid (5.853 g, 22 mmol), K_3PO_4 (20.0 g, 95 mmol) and dioxane (300 mL) were combined in a three-necked flask and stirred in an oil bath equipped with a magnetic stirrer. The mixture was then bubbled with argon for 30 min. Then the mixture was degassed on the

Schlenk line and was refilled with argon. $Pd(PPh_3)_4$ (500 mg, 0.43 mmol) were introduced into the flask under argon atmosphere. When mixed well, the mixture was heated with stirring at 90 °C for 72 h. After cooling to ambient temperature, the mixture was filtered and washed with chloroform for three times. The filtrate was combined with chloroform and evaporated under vacuum. The resulting gray oil was then dissolved with few amount of chloroform and was purified by silica gel column. The petroleum/ethyl acetate (3/1) was used as the elute. After removing the organic solvents, white solid was obtained (yield: 3.21 g, 52 %). The resulting product is the ester derivative of the target ligand.

The carboxylate ester was hydrolyzed with NaOH. After the ester was dissolved in the solution of THF/EtOH/H_2O (2/2/3, 250 mL), NaOH (12 g, 300 mmol) was added into the solution. The mixture was then refluxed in 100 ^{o}C for 12 h. After cooling to room temperature, the mixture was acidified with concentrated HCl. A white precipitate was obtained. The white powder was then filtered, washed with water and dried under 60^{o}C in a vacuum oven (1.06 g, 45.3 %). The resulting $H_5\mathbf{L}$ was confirmed by the ^1H NMR spectrum (Fig. S2).

(b) Complex 1

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (24 mg, 0.1 mmol) and $H_5\mathbf{L}$(10 mg) was dissolved in 4 mL DMA/H_2O mixed solvent (v/v = 1/1), and then 0.1ml CF_3COOH was added. All the reagents were sealed in a glass bottle and slowly heated to 85°C from room temperature in 400 min. After keeping at 85°C for 3000 min, the mixture was slowly cooled to 30°C at a rate of 7°C/h. The Pale-blue block crystals could be collected after washed with DMA and dried in the air. The sample of **1** in 71% yield based on copper was insoluble in common solvent such as H_2O, dichloromethane or methanol.

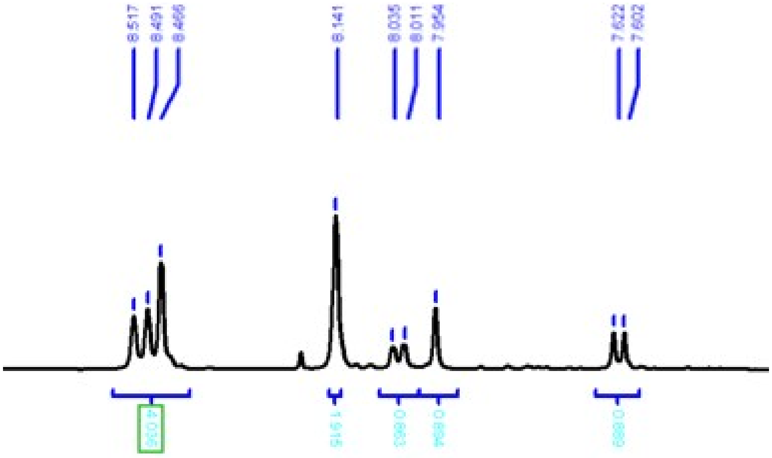


Fig. S2 ^{1}H NMR spectrum of **H_5L** in d_6-DMSO.

1.2 Crystal data of complex 1

Table S1 Crystal data and structure refinement for complex 1

Compound	1
Formula	$C_{39}Cu_2O_{17}H_{60}N_5$
M	998
Crystal system	Trigonal
Space group	*R-3m*
a/Å	18.6883(4)
b/Å	18.6883(4)
c/Å	38.1776(9)
α/deg	90.0
β/deg	90.0
γ/deg	120.0
V/Å^3	11547.3(4)
Z	18
GOF	4.752
$R_1{}^a/wR_2{}^b$ $I > 2\sigma(I)$	0.1241,0.4082
R_1, wR_2 (all data)	0.1299,0.4273
R_{int}	0.0189

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{0.5}$.

1.3 Determination of single-crystal structure

Single crystal of the prepared complex with appropriate dimensions was chosen under an optical microscope and quickly coated with high vacuum grease (Dow Corning Corporation) before being mounted on a glass fiber for data collection. Data for **1** were collected on Super Nova diffractometer equipped with a Cu-K_α radiation X-ray sources (λ = 0.71073 Å) and an Eos CCD detector under 100 K. The data were collected with a ω-scan technique and an arbitrary φ-angle. Data reduction was performed with the CrysAlisPro package, and an analytical absorption correction was performed. The structures were treated anisotropically, whereas the aromatic and hydroxy-hydrogen atoms were placed in calculated ideal positions and refined as riding on their respective carbon or oxygen atoms. Structure was examined using the Addsym subroutine of PLATON[2] to assure that no additional symmetry could be applied to the models.

1.4 Adsorption of dye molecules

The freshly prepared sample **1** was immersed in aqueous solutions containing dye molecules such as methylene blue (MB), crystal violet (CV), rhodamine B (RB) and methyl orange (MO^-) to test the adsorption capacity of **1**. The concentration of all the dye molecules was 4×10^{-5} mol/L.

1.5 A typical procedure for the adsorption experiments

Before adsorption, **1** was dried overnight under vacuum at 100°C and kept in a desiccator. Then the adsorbent (5 mg) was weighed precisely. During the adsorption process, adsorbent (5 mg) was used for the removal of MB with the concentrations of 4×10^{-5} M. The dye solutions (5 ml) containing the adsorbents were maintained for a fixed time (10 min to 12 h) at 25°C. The solution was separated from the adsorbent. The dye concentrations were calculated by comparing the UV-vis absorbance (at λ=665 nm) of the dye solutions containing the adsorbents for a fixed time to that of the original dye solution.

1.6 Computational methods

Density functional theory (DFT) calculations: DFT calculations were performed to provide the atomic partial charges of framework **1** for the grand canonical Monte Carlo (GCMC) calculations as well as give the optimized structures and energies of methylene blue (MB) interaction with the frameworks of **1** and NOTT-101. We used the PW91 functional with the double-ξ numerical polarization (DNP) basis set implemented in the DMol^3 program package in the Materials Studio of Accelrys Inc. for our calculations. Fragmented cluster models were cleaved from the unit cells for modeling the partial charges, structures and energies, because calculations using the whole unit cells are too expensive. The cleaved bonds at the boundaries of the clusters were saturated by protons. Also, the counterion $(CH_3)_2NH_2^+$ was included to make the calculation model closer to the reality (see Fig. S7). The tolerances of energy, gradient and displacement convergence were 1×10^{-5}hartree, 2×10^{-3}hartree/Å, and 5×10^{-3} Å, respectively. The atomic charges in complex **1** (Table S2) were estimated by fitting to the electrostatic potential (ESP) obtained with the CHELPG method,[3] which has already successfully used to describe the behavior of other MOFs.[4] The adsorption energies (ΔE_{ad}) of MB interaction with the frameworks of **1** and NOTT-101 were calculated by $\Delta E_{ad} = E_{MB} + E_{cluster} - E_{MB\text{-}cluster}$, where E_{MB}, $E_{cluster}$ and $E_{MB\text{-}cluster}$ are the total energies of the MB molecule, the fragmented cluster and the adsorption system at their optimized geometries, respectively.

Grand Canonical Monte Carlo (GCMC) calulations: In this work, the low-pressure and high-pressure adsorption isotherms of pure CO_2, CH_4 and N_2 in **1** were simulated using the GCMC method. All simulations were performed with the Monte Carlo simulation suite of the MUSIC code. Periodic boundary conditions were applied in three dimensions. The framework was rigid during simulation considering the negligible influence of framework flexibility on the adsorption of gases under the low-energy conditions.[5] The cutoff distance for truncation of the intermolecular (LJ) interactions was set to 8 Å, and the Ewald sum technique was used to compute the electrostatic interaction. During the simulations, the number of trial moves was 2×10^7. The first 10^7 moves were used for equilibration, and the subsequent 10^7 moves were performed to sample the desired properties.

CO_2 was modeled as a rigid linear molecule with three charged LJ interaction sites, and the LJ potential parameters were taken from the TraPPE model, which were developed by Potoff, Siepmann,[6] and Sun.[7] Theatomic partial charges of the framework of **1** were taken from our DFT results (Table S2), and were adjusted slightly to make the whole system maintain charge neutrality. N_2 was represented as a rigid three-site model with two sites located at N atoms and third one located at its center of mass (COM). CH_4 was represented as a rigid five-site model, which were developed by Siepmann[8] and Kollman.[9] All the interaction parameters conform to Lorentz−Berthelot mixing rules, i.e., $\varepsilon_{ij}= (\varepsilon_{ii}\varepsilon_{jj})^{1/2}$, $\sigma_{ij} = (\sigma_{ii} +$

σ_{jj})/2, and a combination of site−site LJ[10] and Coulombic potentials was used to calculate the intermolecular interaction and the gas−framework interaction. The site−site LJ potential was described by the LJ (12, 6) model, and the electrostatic interaction was calculated via the Coulomb law.

Molecular Dynamics (MD) Calculations: The structures of the MB and rhodamine B (RB) molecules in the pore of **1** were optimized using Forcite in Materials Studio of Accelrys Inc. The interatomic interactions are described by the force field of a condensed-phase optimized molecular potential for atomistic simulation studies (UFF). The cutoff distance for truncation of the intermolecular interactions was set to 1.28 nm, and the Ewald sum technique was used to calculate the electrostatic interaction.

2. IR spectra of 1

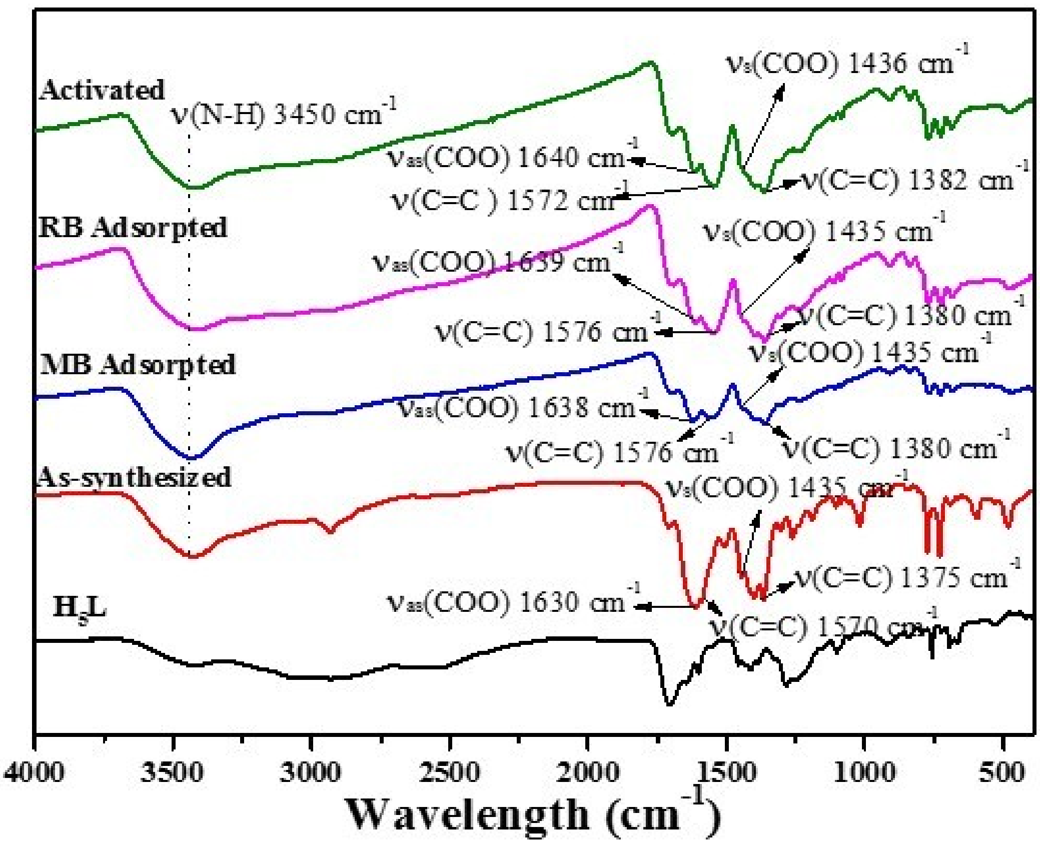


Fig. S3 FT-IR spectra of the ligand H_5L and **1** at the as-synthesized, activated, MB^+ and RB^+ adsorbed states.

3. The TG curve of 1

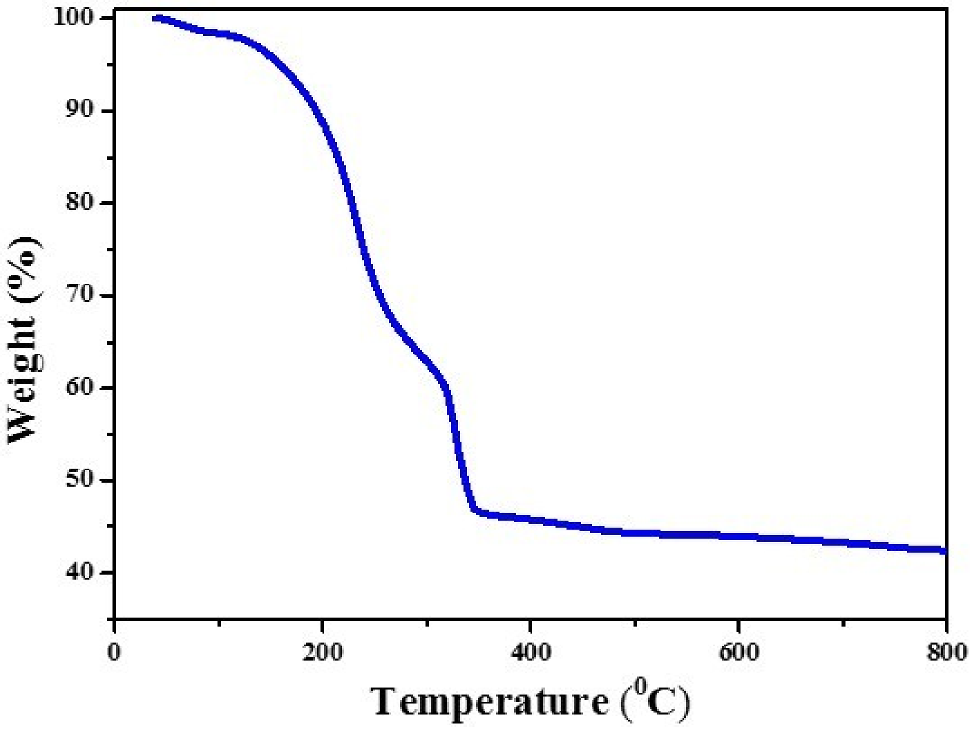


Fig. S4 TG curve of **1.**

4. The gas adsorption of 1

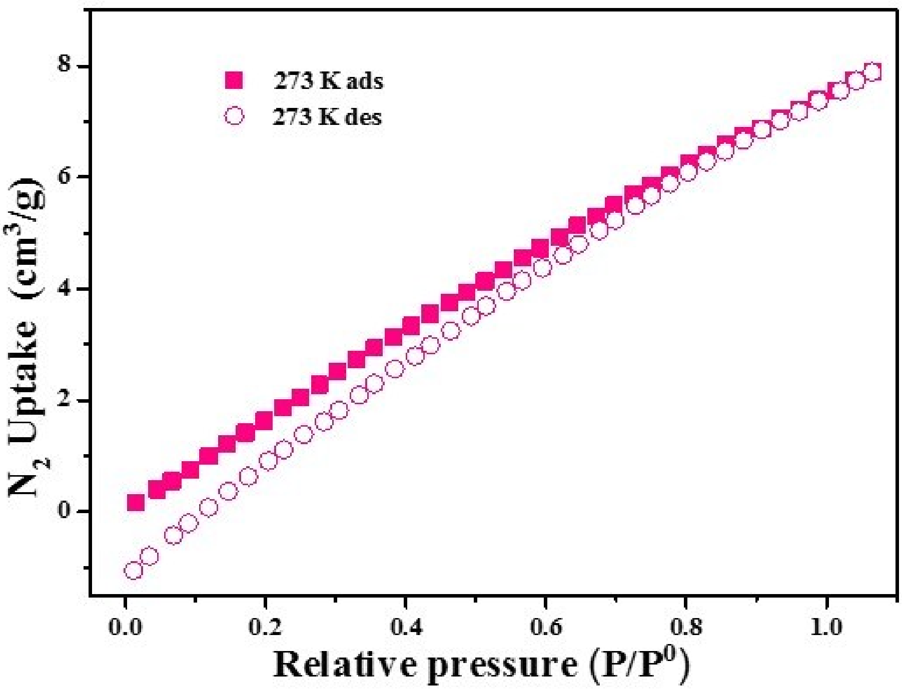


Fig. S5 N$_2$ adsorption isotherms of complex **1.**

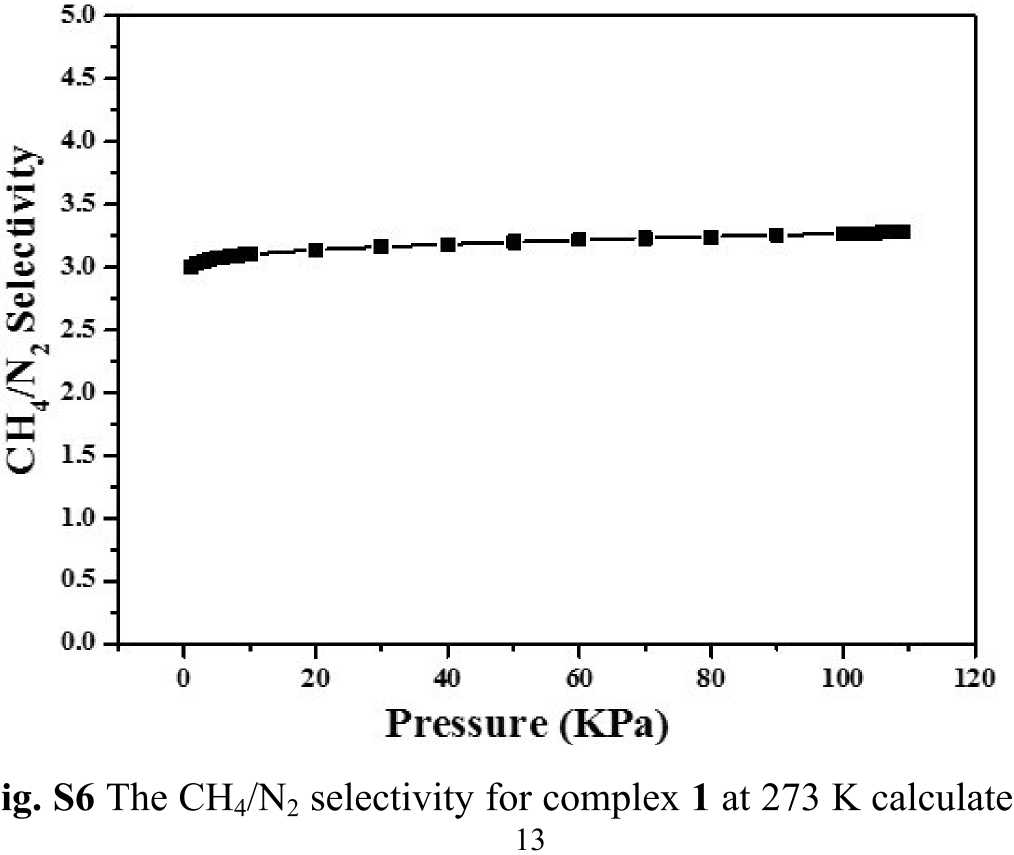


Fig. S6 The CH$_4$/N$_2$ selectivity for complex **1** at 273 K calculated by the IAST method for concentration 50/50 in the CH_4/N_2 binary mixture.

5. Molecular simulation (GCMC) for 1

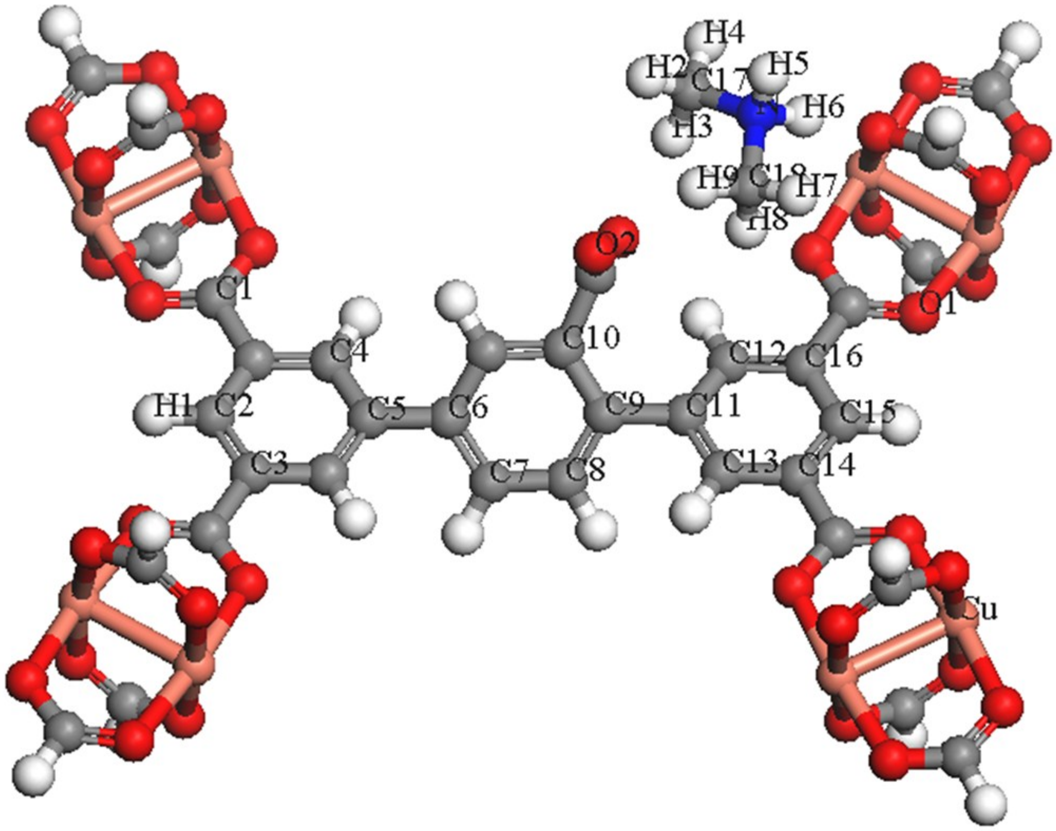


Fig. S7 Atomic representations of complex **1.**

Table S2. Partial charges and the corresponding atom types in complex **1**

Atom	Charge	Atom	Charge	Atom	Charge
O1	-0.571	C10	-0.069	H1	0.167
O2	-0.566	C11	0.055	H2	0.175
C1	0.640	C12	-0.131	H3	0.172
C2	-0.20	C13	-0.193	H4	0.257
C3	0.036	C14	0.013	H5	0.247
C4	-0.208	C15	-0.21	H6	0.128
C5	0.085	C16	-0.029	H7	0.175
C6	0.140	C17	-0.472	H8	0.179
C7	-0.222	C18	-0.514	H9	0.257
C8	-0.147	Cu	0.901		
C9	0.064	N	0.152		

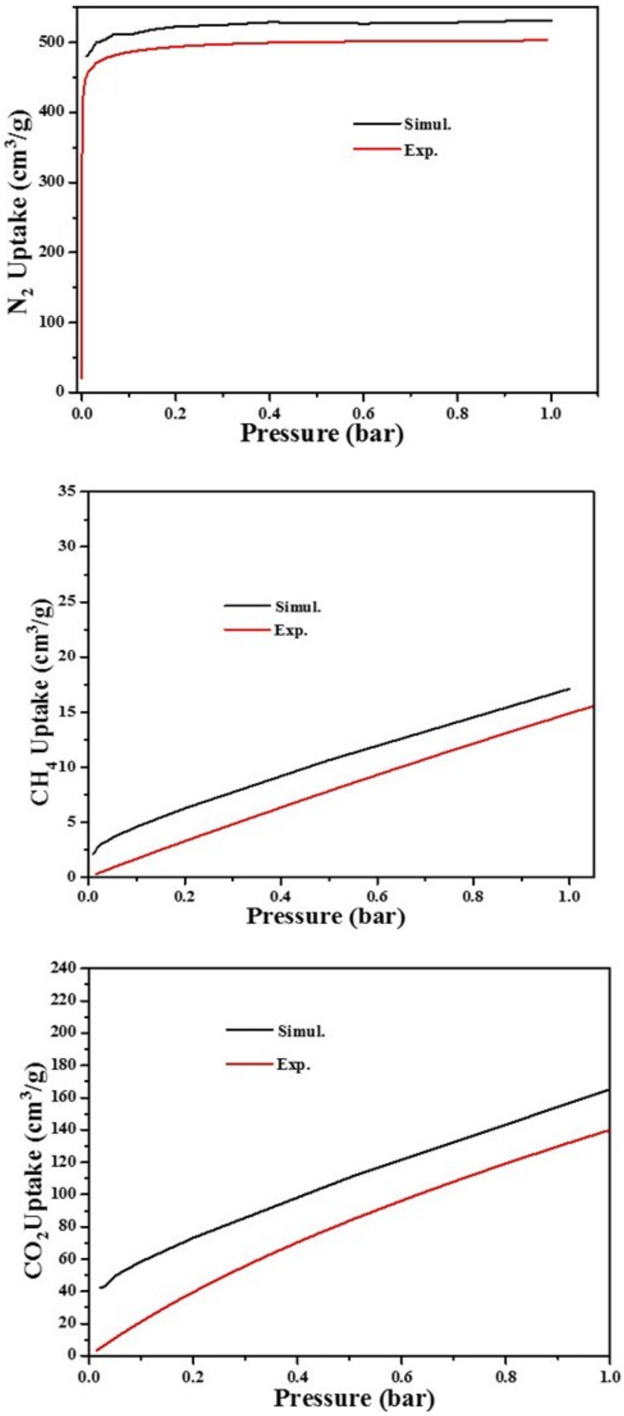
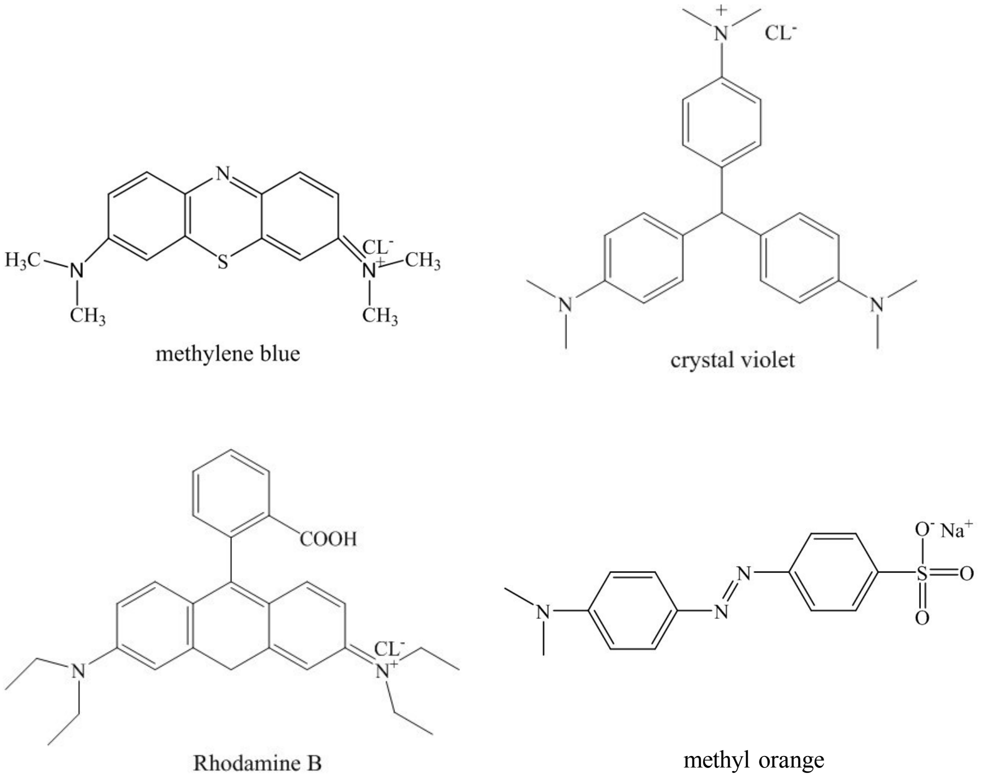


Fig. S8 The simulated and experimental excess adsorption isotherms of N_2 (77 K), CH_4 (295 K) and CO_2 (273 K) in **1.**

6. UV-Vis spectra of 1



methylene blue

crystal violet

Rhodamine B

methyl orange

Fig. S9 The structural formula of the dye molecules studied.

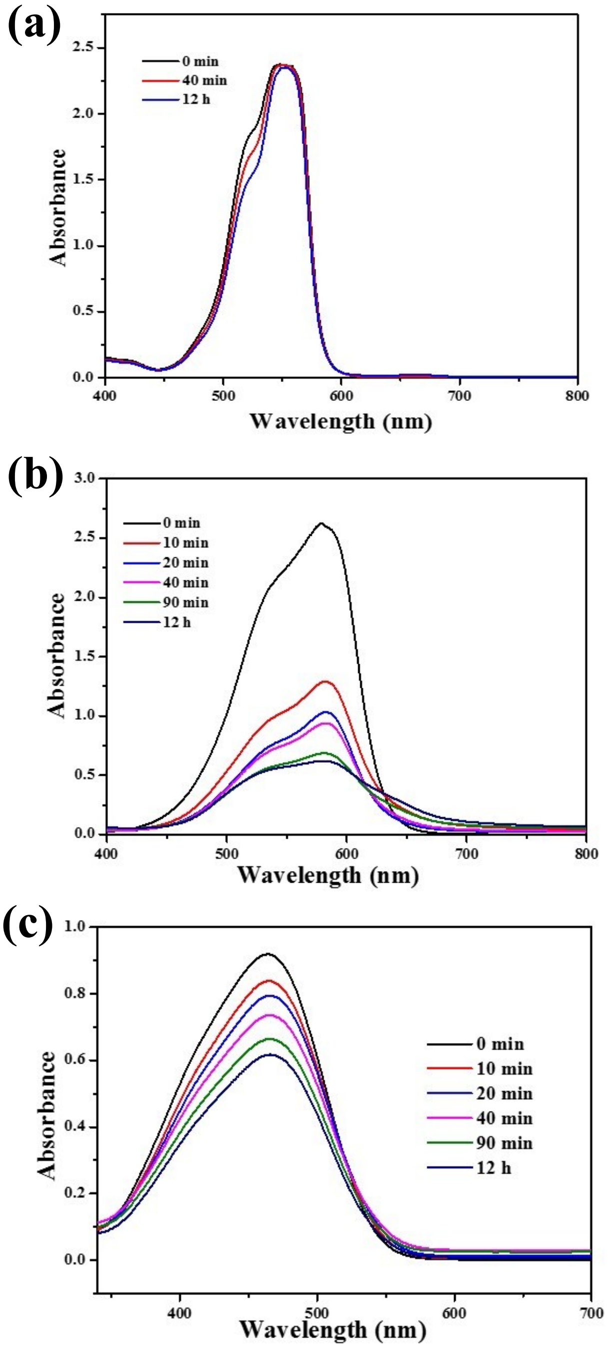


Fig. S10 (a) UV-Vis spectra of the RB^+ aqueous solution during an adsorption test with **1** over 0 min, 40 min and 12 h. (b) UV-Vis spectra of the CV^+ aqueous solution during an adsorption test with **1** over 0 min, 10 min, 20 min, 40 min, 90 min and 12 h. (c) UV-Vis spectra of the MO^- aqueous solution during an adsorption test with **1** over 0 min, 10 min, 20 min, 40 min, 90 min and 12 h.

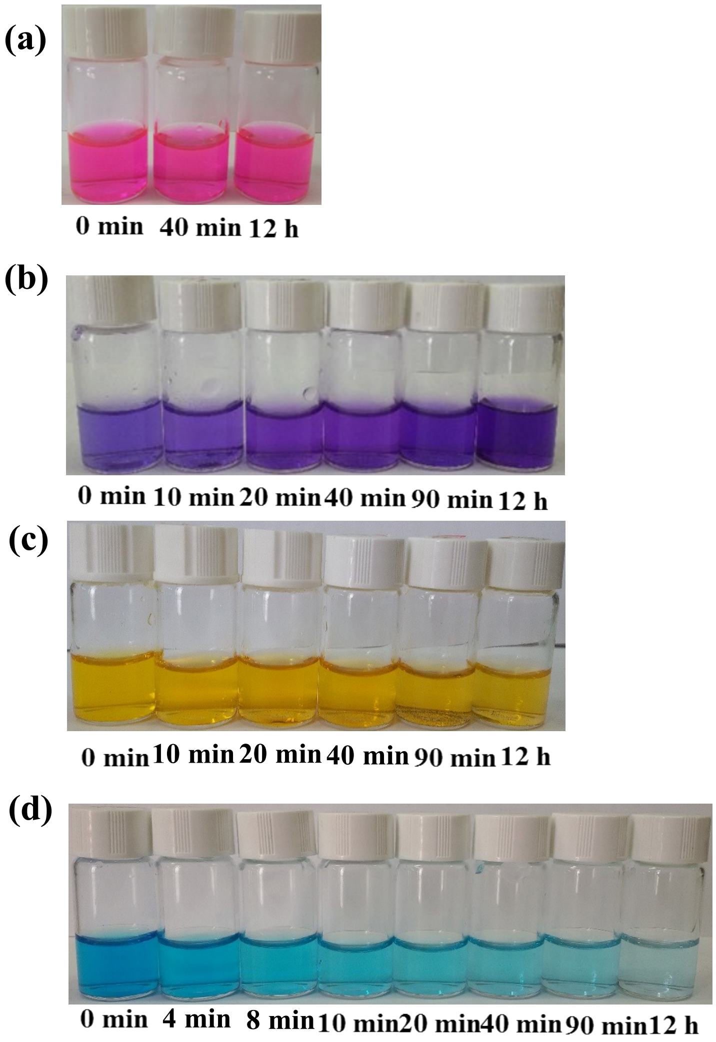


Fig. S11 (a) Photographs of the RB^+ aqueous solution during an adsorption test with **1** over 0, 40 min and 12 h. (b) Photographs of the CV^+ aqueous solution during an adsorption test with **1** over 0, 10 min, 20 min, 40 min, 90 min and 12 h. (c) Photographs of the MO^- aqueous solution during an adsorption test with **1** over 0, 10 min, 20 min, 40 min, 90 min and 12 h. (d) Photographs of the removal of MB^+ in H_2O with **1** over 0, 4 min, 8 min, 10 min, 20 min, 40 min, 90 min and 12 h.

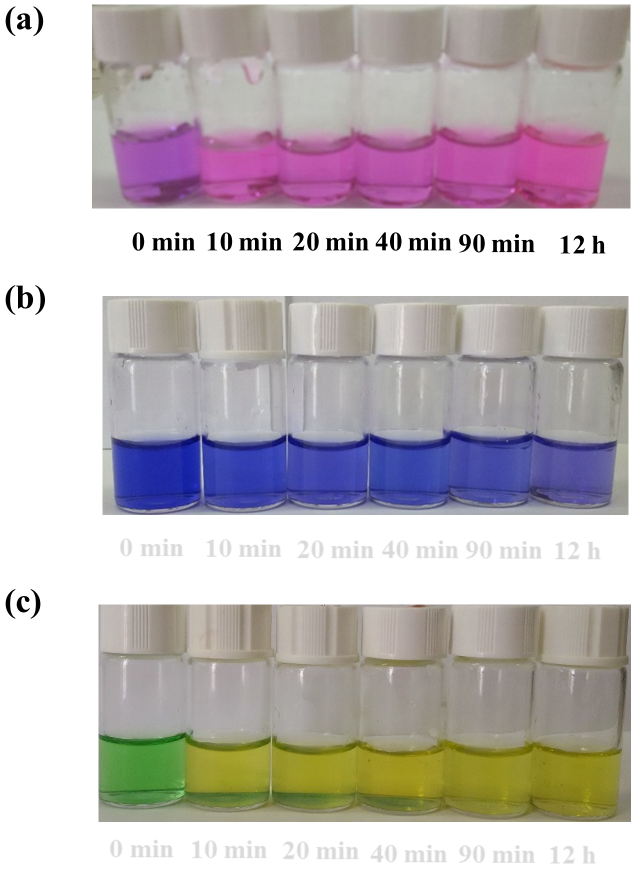


Fig. S12 Photographs of the removal of (a) MB^+/RB^+ (1:1), (b) MB^+/CV^+ (1:1) and (c) MB^+/MO^- (1:1) dye mixtures in H_2O with **1** over 0 min, 10 min, 20 min, 40 min, 90 min and 12 h.

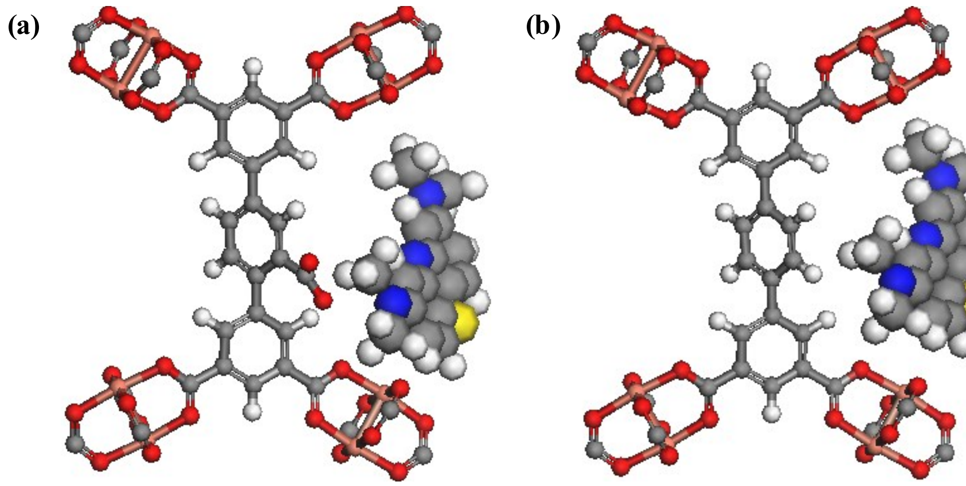


Fig. S13 The adsorbed structures of MB$^+$ in MOFs optimized by the DFT calculations: (a) **1**. (b) NOTT-101.

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